

FINAL TECHNICAL REPORT

Cooperative Agreement NCC 2-957

***Physical and Chemical Study of Minerals and Rocks Containing Low-Z
Compounds of Interest to Astrobiology and Origin of Life***

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Abstract

Understanding the origins of Life requires a good understanding of the physics and chemistry of biogenic low-z elements H, C, N, O, P, S in terrestrial environments, on Mars, on extraterrestrial bodies such as meteorite parent bodies and comets, and in interstellar space. In this Proposal five Tasks form a coherent program aimed at elucidating various aspects of low-z element geo- and cosmochemistry with special reference to the origin of Life on Earth and to the search for life on Mars, extant or extinct.

- (i) Formation of organic molecules, in particular oxygenated H-C-O molecules or precursors thereof of the composition $H_xC_yO_z^{n-}$, inside the hard matrix of structurally dense magmatic minerals;
- (ii) Formation of organic molecules inside the soft matrix of amorphous and crystalline water ice;
- (iii) Preservation of organic molecules in cherts and other siliceous rocks formed in hot spring or submarine hydrothermal vent environments;
- (iv) The nature of the elusive Martian soil oxidant; and
- (v) Prototype development of an XRD instrument, using a new patented XRD camera concept that utilizes a Charge Coupled Device (CCD) as a camera and as a energy-dispersive analyzer.

Overview

Understanding the origins of Life requires a good understanding of the physics and chemistry of biogenic low-z elements H, C, N, O, P, S in terrestrial environments, on Mars, on other extraterrestrial bodies such as meteorite parent bodies and comets, and in interstellar space.

The five Tasks of this Cooperative Agreement form a coherent program aimed at elucidating various aspects of low-z element geo- and cosmochemistry with special reference to the origin of Life on Earth and to the search for life on Mars, extant or extinct.

- 1) Formation of organic molecules, in particular oxygenated HCO molecules or precursors thereof, $H_xC_yO_z^{n-}$, inside the hard matrix of structurally dense magmatic minerals;
- 2) Formation of organic molecules inside the soft matrix of amorphous and crystalline water ice and their preservation in interstellar and planetary ices.
- 3) Preservation of organic molecules in cherts and other siliceous rocks formed in hot spring or submarine hydrothermal vent environments;
- 4) Nature of the elusive Martian soil oxidant; and
- 5) Prototype development of an XRD/XRF instrument, using a new patented XRD camera concept utilizing a Charge Coupled Device (CCD) as a camera and as a energy-dispersive analyzer.

- (i) Task 1 is concerned with the formation of complex organic molecules, in particular, oxygenated H-C-O molecules or precursors of the general composition $H_xC_yO_z^{n-}$, inside the "hard" matrix of structurally dense magmatic minerals. The formation of these organic molecules is believed to occur through a series of reaction steps in the solid state, comprising the dissolution of H_2O and CO_2 in magmatic minerals during their crystallization from an H_2O/CO_2 saturated melt, a redox conversion of solute H_2O and CO_2 into H_2 plus reduced C, and the formation of $H_xC_yO_z^{n-}$ precursors through segregation of H_2 plus reduced C toward dislocations, grain and subgrain boundaries, and other major defects. Evidence for such $H_xC_yO_z^{n-}$ precursors has been obtained through a stepwise extraction study of crushed synthetic MgO single crystals and crushed San Carlos, AZ, olivine single crystals from the upper mantle. The analytical tools employed include thin layer chromatography (TLC), infrared (IR), proton and carbon nuclear magnetic resonance (1H -NMR and ^{13}C -NMR) spectroscopy, and gas chromatography - mass spectroscopy (GC-MS).
- (ii) Task 2 is concerned with the formation of organic molecules in the "soft" matrix of amorphous and crystalline water ice. This work is of special interest to Astrobiology because of the well-documented occurrence of numerous organic compounds in the interstellar space. Interstellar dust particles, comets and planetesimals that formed in the solar nebula have long been proposed to have acted as carriers of organic matter during the period of heavy bombardment during the Earth's early history. The in-fall of comets might have contributed significantly to the inventory of available organic matter from which Life sprang. The work centers on ice as an analog for comets and ice mantle around dust nucleation centers. It aims at understanding the physical and chemical properties of amorphous water ice condensed at

low temperatures, either as pure compound or in the presence of various gases, and during warm-up and recrystallization. The analytical tools employed involve mainly transmission electron microscopy, electron energy loss spectroscopy (EELS), x-ray diffraction (XRD) and infrared (IR) spectroscopy.

- (iii) Task 3 is concerned with the preservation of organic molecules that became included in cherts and other rocks formed by secondary processes at the surface of the Earth or in submarine hydrothermal vents. Prominent among these rocks are forms of silica which precipitate out of hot springs, carbonates, diagenetically formed phosphates, and sulfides from submarine "smokers". The emphasis is placed on understanding the short-, mid- and long-term survivability of organic matter encapsulated in these rocks with 'long-term' meaning periods spanning billions of years, going back to the oldest biochemical fossil records on terrestrial rocks. This work has relevance to NASA's missions to Mars. One major exobiological task will be to identify areas on the surface of Mars where hot spring activity did occur in the distant past. Such hot spring environments may have harbored forms of life that developed on Mars during a period of different climatological constraints. To help with the landing site selection for Mars missions it is crucial that all aspects of the preservation of organic matter in such local environments be well understood. The tools on this research comprise optical microscopy of petrological thin sections, Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF) spectroscopy. The ability to distinguish high-temperature stromatolites that formed in the presence of hyperthermophilic biofilms from demonstrably abiotic precipitates with similar stromatolite-like structures is crucial with regard to the identification of biogenicity. Previous studies by Cady and co-workers (1995; 1996) have shown that along the margins of near-boiling springs in Yellowstone, microbial biofilms that contain hyperthermophiles contribute to the microstructural development of high-temperature siliceous sinters. Because it is likely that all high-temperature subaerial siliceous sinters will have formed in the presence of hyperthermophilic biofilms, these types of deposits will be produced experimentally using a precipitation chamber attached to an aseptic geothermal well pipeline at the Wairakei power station, Taupo, New Zealand. The experimental abiotic sinters will then be compared to biogenic sinters precipitated at the same temperatures from a similar mother fluid that sources nearby thermal springs. It is expected that the results of this comparative study will provide a new set of criteria which will enhance our ability to recognize biogenicity in high-temperature siliceous sinters, and in other types of deposits that formed in the presence of microbial biofilms.
- (iv) Task 4 is concerned with the Martian soil oxidant. Discovered during the Viking missions, the Martian soil oxidant may be responsible for the absence of detectable organic matter in the Martian top soil. Its nature is not understood. It has been suggested that molecular H_2O_2 , formed by photolysis from H_2O in the Martian atmosphere, may have condensed onto soil grains, producing a highly reactive veneer which would also be thermally labile. Alternatively, the oxidant may derive from within the minerals that constitute the soil. New experimental evidence has shown that magmatic minerals can acquire oxidizing surfaces due to positive holes (O^+ radicals). Such O^+ can be generated from peroxy defects (O_2^{2-}) in the bulk, either thermally, by UV-induced dissociation, or by acoustic waves generated through mechanical fracture. Charge Distribution Analysis (CDA) studies have begun on igneous and highly metamorphosed rocks endorsed by NIST as a "*new technique for measuring previously unmeasurable fundamental properties of materials*". CDA is uniquely capable of distinguishing between a thin surface veneer of H_2O_2 molecules that condensed from the vapor phase, and O^+ surface radicals generated inside the mineral matrices.
- (v) Task 5 is concerned with the prototype development of an XRD instrument, using a new patented XRD camera design. The new design utilizes a Charge Coupled Device (CCD) both as a camera and as an energy-dispersive analyzer, and allows for simultaneous XRD and

XRF analysis. The principal application of such a XRD/XRF instrument is in the determination of the mineralogy and elemental composition of wind-blown dust and unconsolidated soil on Mars and of dust particles collected from a comet. The instrument is intended for inclusion in missions to Mars subsequent to the Mars Pathfinder and Russian Mars '98 missions. The instrument would additionally be useful for general mineralogical analysis during future landed missions on solar system bodies such as comets, asteroids and satellites of the outer planets. The instrument uses $\text{CuK}\alpha$ radiation and Bremsstrahlen below the K absorption edge of Cu. Its geometry is similar to a microfocus X-ray camera with the sample being placed between X-ray source and CCD detector. The detector intersects diffraction angles from almost 0° to $50^\circ 2\theta$, which include definitive diffraction maxima for nearly all minerals of potential interest. Quantitative analysis will be performed by Rietveld analysis. In the feasibility study, we will:

- (i) utilize a CCD and laboratory X-ray generator (with a Cu tube) to collect and evaluate diffraction patterns and fluorescent spectra of mineral standards and Mars analog samples;
- (ii) Compare data from 1 above with data obtained from the same samples utilizing conventional XRD and XRF laboratory equipment; and
- (iii) construct a breadboard instrument based on the results of the feasibility study.

Task 1.

Organic Matter formed in and Extracted from Magmatic Crystals

We demonstrated that short to medium chain length carboxylic and dicarboxylic acids as well as N-bearing organic compounds can be extracted from crystals grown from $\text{CO}_2/\text{H}_2\text{O}/\text{N}_2$ -saturated melts or magmas and dissolved traces of the gas/fluid phase components CO/CO_2 , H_2O and N_2 . We work with MgO , a cubic oxide with a very high melting point, 2860°C and a densely packed structure, and with olivine crystals, $(\text{Mg,Fe})_2\text{SiO}_4$, from the San Carlos, AZ, locality which originate from the high CO_2 - H_2O pressure environment of the upper mantle.

Batches of about 50 g of single crystals were externally cleaned with CHCl_3 in a glass Soxhlet apparatus (prebaked at 450°C for 10 hrs), using cellulose thimbles precleaned with CHCl_3 . The crystals were then crushed manually in a porcelain mortar (prebaked at 450°C for 10 hrs) to a medium fine powder. The powder samples were Soxhlet-extracted with three solvents (250 ml, 14-16 hrs each) of increasing polarity: first chloroform, then acetone, and finally tetrahydrofuran (THF). Full procedural blanks were performed using the same glassware, an empty thimble or a thimble filled with crushed glass beads, and identical amounts of all three solvents. Similarly, H_2O extraction experiments were performed by placing 20 g of crushed MgO and olivine crystals in glass flasks (prebaked at 450°C for 10 hrs) in 150 ml H_2O , triple-distilled in a sub-boiling fused silica apparatus. The slurries were stirred at 20°C for 30 hrs, with brief periods of sonication, two exchanges of the supernatant 100 ml H_2O , and centrifugation. The combined supernatants were concentrated to about 2 ml by rotary evaporation. To remove cations, the concentrates were passed through a 3×95 mm ion exchange column (AG 50-X 8 resin, 200-400 mesh, H^+ form; Bio-Rad Laboratories, Hercules, CA), prewashed several times with HCl , NaOH solution and H_2O . The column was eluted with 150 ml H_2O , 100 ml 3.5 M NH_4OH and again 150 ml H_2O . The elute was concentrated by rotary evaporation and dried in a desiccator over NaOH . Full procedural blanks were performed with the same ion exchange column and same amounts of H_2O , acid, NaOH and NH_4OH solutions. The THF and H_2O extracts were characterized by infrared (IR), proton nuclear magnetic resonance (^1H -NMR), and gas chromatography-mass spectroscopy (GC-MS) using direct probe insertion techniques and *tert*-butyldimethylsilyl (*t*-BDMS) derivatives.

Gas chromatographic-mass spectroscopic (GC-MS) analysis was performed on the *t*-BDMS derivatives of the THF extracts from MgO and olivine samples. The *t*-BDMS derivatives of the THF extract from MgO were identified on the basis of GC-MS data as oxalic acid, HOCCOOH , glycolic acid, HOCH_2COOH , malonic acid, $\text{HOOC}-\text{CH}_2-\text{COOH}$, and succinic acid, $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{COOH}$. The compounds in the THF extract from olivine were identified as $\text{CH}_2=\text{CH}_2$ -terminated alkyls with up to 11 carbon, those in the *t*-BDMS derivatives as monocarboxylic or fatty acids with up to 12 carbon. Urea was an N-bearing compound extracted from MgO , glycolamide, an N-bearing compound extracted from olivine. Analysis of the vesicular basalt which had brought the olivine crystals from mantle depth yielded no organics, even though such a rock with a large internal and external surface would have been very prone to field contamination. The absence of organics in the basal is a clear indication that, to the extent it might have occurred, field contamination did not affect the extraction results of organics from the crushed olivine crystals. Procedural blanks confirmed no, or negligible, laboratory contamination.

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Task 2.

Ultrastructural and Microchemical Investigation of Extraterrestrial Ice Analogs

We have completed hardware and software improvements to the imaging system so that diffraction patterns can be collected on-line in real time. As a result, we can now collect hundreds of patterns at the rate of one every few seconds, and store the resulting images, which are about 0.5 mb in size, on an optical storage device. We have written software which reduces the two-dimensional diffraction patterns to one-dimensional radial intensity functions. These intensity vs. radial distance functions are calibrated using an internal crystalline gold standard, and a carbon background is subtracted to represent the 20 =C5 carbon substrate. Then, an atomic scattering background is subtracted to yield a diffracted intensity distribution in reciprocal space. A computer program specially written for this application finds the maxima in the background-subtracted patterns and fits Gaussian peaks to each. Various derived parameters (peak position in k space, peak width, integrated intensity, peak height, etc. can then be plotted as a function of temperature. When some crystallinity exists in the pattern, a percentage of crystalline material is subtracted (using previously collected diffraction patterns of crystalline materials) to yield the residual amorphous pattern and then the amorphous maxima are measured. Using data such as these, nearly imperceptible changes in the structure of the ice can be quantitatively measured.

From this technique a number of important discoveries were made. Jenniskens and Blake (1994) were finally able to confirm the existence of the high-density vapor deposited form. Later experiments using X-ray diffraction had proven inconclusive because of the inability to grow slowly enough the thick ice layers that are needed for this technique. It was found that there is a well-defined transition between the high and low density amorphous form, and the form change was related to published gas trapping/gas release and radical diffusion data in the temperature regime of 15 to 80 K, which provided the first evidence for a structural basis for these phenomena. We further studied the deposition conditions necessary for the creation of this form, the expected time dependence, and performed molecular dynamics calculations to simulate the high-density ice structure. It was found that the ice typically lacks the open cages that prevail in crystalline ice and its amorphised counterpart, the low-density amorphous form. Some explanations were given for the markedly different physical properties of this high density amorphous form in terms of behaviour during electron beam processing and viscosity upon irradiation. It was found that most of the ice frozen on interstellar grains is in this form and implications for the formation of organic matter on grains were given.

Other important advances relate to the behaviour of water ice at high temperature. We investigated the crystallization behaviour of water and discovered that the crystallization rates imply that the liquid form of water found just above the glass transition is a strong liquid, characterized by a viscosity behaviour that is well expressed by an Arrhenius law with a single activation energy barrier. That is the first direct evidence that this liquid form of water differs markedly from normal liquid water at high temperatures, which is a "fragile" liquid, with the property of keeping a very low viscosity during cooling from higher temperatures and a rapid decrease of viscosity just above the glass transition temperature. We discussed the interesting implications of the strong/liquid character of the ice for the crystallization behaviour of both pure and impure ices in the solar system. Crystallization is thought to be a process that underlays the outgassing of comets and has implications for the volatile retention in solar system ices, an important issue in illuminating the composition of comets, which determines the supply of organic matter to the early Earth.

With that, we had thought to have more or less fully characterized the pure water ice system in the temperature range of 15-180 K for vapor-deposited ices. It was found however, that around 175 K an interesting morphology change occurs in the water ice films. The first indication of this was given by the discovery that an amorphous component is always present in the diffraction patterns of

our ice films in the cubic regime, even when crystallization has completely stopped. A more detailed study of morphological properties of the ice film, in combination with Temperature-Programmed-Desorption and grazing angle RAIRS studies done elsewhere, provided the first evidence that the bulk viscosity of the restrained amorphous form indeed goes down above the glass transition temperature, but also that the viscosity continues to decline until at least 175K. The presence of this liquid form in such a broad range of temperatures (150-200K) implies that this form is abundant in nature, for instance in the subsurface of comets and the surfaces of planets and their satellites.

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Task 3.

Thermal Spring Environments as Analogs for Early Life on Earth and Site Selection for Mars Exopaleontology

An important goal of NASA's exobiology program is to understand the early evolution of the biosphere on Earth. Thermal spring environments are regarded as important environments for early life on Earth. Molecular phylogenies constructed for living organisms on Earth reveal that extreme thermophiles (organisms that prefer high temperatures exceeding $>80^{\circ}\text{C}$) lie in primitive positions in the universal tree of life. Thus, hydrothermal systems are likely to have been key habitats for early life, and some scientists believe that life actually originated there. Certainly from a geological standpoint it is quite likely that hydrothermal environments were widespread on the early Earth. The heat flow was much higher on the early Earth, and volcanism more widespread. The same is likely to have been true on Mars. To date, few examples of hydrothermal deposits have been recognized in ancient rock sequences on Earth, largely because we don't yet know how to recognize them. Studies of modern and sub-Recent thermal spring systems are needed to establish criteria for recognizing ancient deposits, and for understanding how to interpret their paleontology. So far, the only well-studied examples are those we have described in this project over the past two years. We believe that detailed paleontological studies of ancient thermal spring deposits will allow us to trace the history of these systems back into the ancient rock record on Earth and discover independent evidence for testing the relationships that have emerged from RNA phylogenies. Studies of fossilization processes in thermal spring environments enable us to understand how biological information is retained in thermal spring deposits, and how variations in temperature or other parameters influence styles of preservation. This information is not only prerequisite for understanding the ancient record on Earth, but also provides information needed to formulate meaningful strategies to explore for ancient life on Mars.

An important aspect of NASA's plan for future missions to Mars focuses on the selection of sites to explore for evidence of ancient life. The Viking biology experiments provided no evidence for extant life on Mars and it is generally agreed today that the most promising approach in exploring for life on Mars, at least in surface environments, is in searching for a record of an ancient Martian biosphere. Because Mars was more Earth-like early in its history (denser atmosphere and abundant liquid water), during the same time that life emerged on Earth (3.0 - 4.0 Ga), it is possible that life arose there as well, becoming extinct in surface environments as Mars lost its atmosphere and began to refrigerate. Thus, future exploration of the Martian surface will focus on the search for evidence of an ancient biosphere. Based on studies of the ancient fossil record on Earth, the most favorable places to search for a fossil record on Mars are geological settings where aqueous minerals are likely to have precipitated under biologically-favorable conditions. Candidate mineral deposits include the deposits of subaerial thermal springs and or cooler subaqueous spring deposits, evaporites, and mineralized subsoils where "hardpans" may have formed. On Earth, such deposits often contain well-preserved microbial fossils, and/or biomolecular compounds of great interest for Mars "exopaleontology".

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Invited Talks

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Task 4.

Charge Distribution Analysis for Planetary Exploration.

The Martian soil oxidant, first discovered during the Viking missions, has a highly destructive effect on organic matter and therefore on any traces of possible Early Life on Mars. One theory suggests that molecular H_2O_2 was formed by photolysis in the thin Martian atmosphere, and condensed onto soil and regolith grains. This produces a highly reactive but also thermally labile surface veneer. In recent years experimental evidence has shown that terrestrial minerals also acquire oxidizing surfaces. The origin of these positive surface charges are positive holes (or O^- radicals), generated from peroxy defects (O_2^{2-}) in the bulk, either thermally or by UV-induced dissociation. This is of direct relevance to the formation of the oxidant in the Martian soil. The peroxy in turn forms during crystallization or solidification of the host material inside nominally anhydrous magmatic minerals from small amounts of H_2O ("water"), incorporated as OH^- . The omnipresence of O^- in terrestrial minerals suggests a common origin to the Mars soil oxidant.

We also studied the generation of highly mobile positive hole-type charge carriers from the peroxy in rocks. Electrical resistivity changes, ground potentials, electromagnetic (EM), and luminous signals preceding or accompanying earthquakes have been reported many times, besides ground uplift and tilt and other parameters. However, no concept exists that would tie these diverse phenomena together into a physically coherent model. Using low to medium velocity impacts to measure electrical signals with μsec time resolution, it is observed that, when gabbro and diorite cores are impacted at relatively low velocities, $\bullet 100 \text{ m/sec}$, highly mobile charge carriers are generated in a small volume near the impact point. They spread through the rocks, causing electric potentials exceeding $+400 \text{ mV}$, EM and light emission. As the charge cloud spreads, the rock becomes momentarily conductive. When a granite block is impacted at higher velocity, $\bullet 1.5 \text{ km/sec}$, the propagation of the P and S waves is registered through the transient piezoelectric response of quartz. After the sound waves have passed, the surface of the granite block becomes positively charged, suggesting the same charge carriers as observed during the low velocity impact experiments, expanding from within the bulk. During the next 2-3 msec the surface potential oscillates, indicating pulses of electrons injected from ground and contact electrodes. The observations are consistent with positive holes, e.g. defect electrons in the O^{2-} sublattice, traveling via the O 2p-dominated valence band of the silicate minerals. The positive holes propagate as charge clouds rather than as classical EM waves. Before activation, they lay dormant in the form of electrically inactive positive hole pairs, PHP, chemically equivalent to peroxy links, $\text{O}_3\text{X}^{\text{OO}}\text{XO}_3$, with $\text{X}=\text{Si}^{4+}$, Al^{3+} etc. PHP's are introduced into the minerals by way of hydroxyl, $\text{O}_3\text{X}-\text{OH}$, which all nominally anhydrous minerals incorporate when crystallizing in H_2O -laden environments. The fact that positive holes can be activated by low energy impacts, and their attendant sound waves, suggests that they can also be activated in the crust by microfractures during the dilatancy phase. Depending on where in the stressed rock volume the charge carriers are activated, they will form rapidly moving or fluctuating charge clouds that can account for earthquake-related electrical signals and EM emission. Wherever such charge clouds intersect the surface, high fields are expected, causing electric discharges and earthquake lights.

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Task 5:

Combined X-Ray Diffraction/X-ray Fluorescence Instrument Development

The instrument development proceeded according to plan. Substantial progress in the performance of the test instrument was achieved.

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